

# Curie temperature control by band parameters tuning in

## $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$

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We present the study of magnetic and transport properties of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$ . AC magnetic susceptibility measurements as well as transport characterization were performed. The obtained results indicate that the presence of two types of magnetic ions influences magnetic properties of investigated IV–VI semimagnetic semiconductor. A qualitative analysis and possible mechanisms of the substantial dependence of the Curie temperature on the Eu content are presented. The most likely reason of the observed Curie temperature behaviour is a strong dependence of the location of a heavy mass  $\Sigma$  band upon the alloy composition. The theoretical calculations in frame of simple models confirm this point.

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## I. INTRODUCTION

Manipulation of the spin degree of freedom in semiconductors has become a focus of interest in recent years. In the context of spin electronics particularly interesting are ferromagnetic and semimagnetic (diluted magnetic) semiconductors (SMSC's). Understanding of the carrier mediated ferromagnetism was initiated by a study of ferromagnetism in IV-VI based SMSC's. In this class of materials, deviations from stoichiometry result in the carrier density sufficiently high to produce strong ferromagnetic interactions between the localized spins. It was shown that in  $\text{Pb}_{1-x-y}\text{Mn}_x\text{Sn}_y\text{Te}$  mixed crystals with high Sn concentration,  $y \geq 0.6$ , the free hole concentration can be varied by means of isothermal annealing in the range between  $10^{20} \div 10^{21} \text{ cm}^{-3}$  [1].

In the present paper, we consider the effect of the presence of two types of magnetic ions incorporated

into semiconductor matrix on magnetic properties of resultant semimagnetic semiconductor. In order to simplify the theoretical description of the investigated magnetic system, two types of magnetic ions were chosen with spin-only ground state: substitutional  $\text{Mn}^{2+}$  possesses  $S = 5/2$ , while  $\text{Eu}^{2+}$ , the second type of magnetic ion, has  $S = 7/2$ . There are several reasons for which the magnetic semiconductors based on lead chalcogenides are ideal materials for such kind of investigations. First, a variety of magnetic properties has been observed in Mn-based IV-VI SMSC's. Second, the characteristic feature are semi-metallic electric properties with the well developed methods of control of carrier concentration.  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  is a unique system in which the interplay between magnetic and electronic properties can be observed and studied. In particular, the carrier induced paramagnet-ferromagnet as well as the ferromagnet-spin glass transitions have been observed [1], [2]. This is due to the combination of an RKKY type of interaction between the magnetic ions with a possibility to manipulate the free carrier concentration. These two features give IV-VI semimagnetic materials the distinguished position within the whole family of semimagnetic semiconductors. The additional advantage is that for the  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Te}$  crystals, the parameters of the energy structure are very well known.

All known Eu-based IV-VI semimagnetic lead chalcogenides with the carrier density (electrons as well as holes) below  $10^{19} \text{ cm}^{-3}$  are paramagnetic down to the temperature  $T=1 \text{ K}$  (similarly to Mn-based compounds). A strongly localized character of 4f orbitals of the rare earth ions results in very weak exchange interactions both between the magnetic ions and between ions and the free carriers. As a result, the  $\text{Sn}_{1-z}\text{Eu}_z\text{Te}$  crystals are not ferromagnetic. The reason of a lack of ferromagnetism in this material is the very small magnitude of sp-f exchange integral.

The objective of this work was to perform the systematic measurements of magnetic AC susceptibility as well as transport characterization of bulk samples of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  multinary alloy. The as-grown as well as annealed samples with different concentrations  $x$  of Mn as well as  $z$  of Eu were investigated. The paramagnet-ferromagnet as well as ferromagnet-spin glass transitions were observed and studied.

## II. SAMPLE PREPARATION AND CHARACTERIZATION

The crystals of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  were grown by the modified Bridgman method. In the present work, the samples coming from several technological processes were investigated. The chemical composition of the samples was determined by X-ray dispersive fluorescence analysis technique with uncertainty of 10%. Typically, the crystals were cut crosswise the growth axis to the 1–2 mm thick slices. The variation of chemical composition along this area is very small (1–2%). The results of chemical analysis of all

investigated  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples are gathered in Table I.

The standard powder X-ray measurements revealed that the investigated samples are single-phase and crystallize in NaCl structure, similarly as nonmagnetic matrix and  $\text{Pb}_{1-x-y}\text{Mn}_x\text{Sn}_y\text{Te}$  semimagnetic semiconductor. The measured values of lattice constants for several  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples are collected in Table II. For comparison, the values of calculated lattice constant for  $\text{Pb}_{1-x-y}\text{Mn}_x\text{Sn}_y\text{Te}$  crystals with analogous content of Mn and Sn are also presented [3]. The introduction of Mn ions into the nonmagnetic matrix of  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  leads to a decrease of the lattice constant of resultant  $\text{Pb}_{1-x-y}\text{Mn}_x\text{Sn}_y\text{Te}$  [4]. The careful inspection of Table II shows that introduction of Eu ions to  $\text{Pb}_{1-x-y}\text{Mn}_x\text{Sn}_y\text{Te}$  lattice leads to an increase of the lattice constant of resultant compound. All the investigated  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples were characterized by means of low magnetic field transport measurements. The aim of the transport characterization was to obtain information about the elementary electric properties of the investigated samples: the type and density of free carriers and their mobility. In the case of IV-VI semimagnetic semiconductors, the carrier concentration is an important parameter since the change of the concentration influences the magnetic behaviour of the material.

The Hall bar samples with typical dimensions of  $8\text{mm} \times 2\text{mm} \times 1\text{mm}$  were used for the transport measurements. The Hall voltage  $V_H$  as well as conductivity voltage  $V_\sigma$  were measured. The electrical contacts were prepared always in the same way. First the surface of the specimens was etched using the solution of  $\text{Br}_2$  and  $\text{HBr}$  in the proportion 1:20. Next, the gold contacts were deposited by use of gold chloride water solution on the polished surface of the samples. Finally, the electrical contacts were made using indium solder and gold wires. Typical resistance of the samples was equal to about  $1\text{ m}\Omega$ . This allowed to apply relatively large current (up to 300 mA). The Hall as well as conductivity measurements were performed at the room and liquid nitrogen temperature. The standard DC six probe technique at the static magnetic field up to 1T were used. In the present paper, only a nominal Hall concentration  $p$  was determined at the room and liquid nitrogen temperature. All the investigated samples occurred to be  $p$  type with the high and almost temperature-independent hole concentration (in the range between  $2 \times 10^{18}\text{ cm}^{-3}$  and  $2 \times 10^{21}\text{ cm}^{-3}$ ). The obtained values of free hole concentration obtained at room temperature are gathered in Table I. Typical values of mobility were in the range of a dozen and a few dozen of  $\text{cm}^2/\text{Vs}$ . The values of carrier concentration, conductivity and mobility were determined with the uncertainty of 15% at the room temperature and 30% at the liquid nitrogen temperature.

### III. MAGNETIC INVESTIGATIONS

In this section, the results of magnetic studies of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples are presented. AC magnetic susceptibility studies in the temperature range 1.3-150 K using a mutual inductance method were carried out. The susceptibility measurements were carried out in AC magnetic field of frequency range 7-10000 Hz and the amplitude not exceeding 5 Oe.

Generally, in the range of high temperatures all IV-VI semimagnetic semiconductors are Curie-Weiss paramagnets with the temperature dependence of the magnetic susceptibility described by the Curie-Weiss law:

$$\chi(T) = C/(T - \Theta), \quad (1)$$

where  $C = g^2 \mu_B^2 S(S+1) N_M$  is the Curie constant and  $k_B \Theta = (1/3) S(S+1) x \sum z_i I(R_i)$  is the paramagnetic Curie temperature (Curie-Weiss temperature). Here,  $N_M$  is the concentration of magnetic ions,  $z_i$  the number of magnetic neighbors on the  $i$ th crystallographic shell,  $I(R_i)$  the exchange integral between the central ion and its  $i$ th magnetic neighbors,  $S$  the spin of the magnetic ion,  $g$  the spin-splitting  $g$ -factor,  $k_B$  the Boltzman constant, and  $\mu_B$  the Bohr magneton.

For all the investigated samples the high temperature behaviour of the inverse low-field susceptibility  $\chi^{-1}$  was nearly linear and all data fit well to the Curie-Weiss law of the form:

$$\chi(T) = C/(T - \Theta) + \chi_{\text{dia}} \quad (2)$$

where  $\chi_{\text{dia}}$  is the susceptibility of the host lattice (all IV-VI semiconductors without magnetic ions are standard diamagnetic materials with the magnetic susceptibility around  $\chi_{\text{dia}} \simeq -3 \times 10^{-7}$  emu/g).

In the case of  $\text{PbMnEuTe}$  crystals, the obtained negative and relatively small values of the paramagnetic Curie-Weiss temperature  $\Theta$  indicate that a weak antiferromagnetic superexchange interaction is a dominant mechanism of the interaction. These results correspond to those reported earlier for  $\text{PbMnTe}$ . The determined values of paramagnetic Curie temperature  $\Theta$  and Curie constant  $C$  are presented in Table I. The inspection of Table I shows that no distinct trends in  $\Theta$  and  $C$  dependence on Eu concentration can be observed. However, it should be stressed that these values are determined with a rather large inaccuracy related to the uncertainty of the chemical compositions of the samples. Figure 1 presents the high temperature part of the inverse AC susceptibility for several  $\text{PbMnEuSnTe}$  and  $\text{SnMnEuTe}$  samples. The fitting procedure (the Curie-Weiss law) revealed the positive values of the Curie-Weiss temperature in this group of IV-VI mixed crystals. This indicates the presence of a ferromagnetic interaction. The obtained values of Curie-Weiss temperature  $\Theta$  and Curie constant  $C$  are shown in Table I. The careful inspection of Table I

allows to notice significant changes of Curie-Weiss temperature with the Eu content. The decrease of the paramagnetic Curie temperature  $\Theta$  with the increase of Eu concentration is clearly visible. The three samples of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$ : 809\_12, 809\_30, 809\_34 are characterized with very similar values of Mn content and concentration of free holes (see Table I). For the Mn concentration equal to around  $x \simeq 0.02$  and free hole concentration  $p = 4 \times 10^{20} \text{ cm}^{-3}$  increase of Eu content from  $z=0.003$  to  $z=0.01$  leads to the decrease of Curie-Weiss temperature from 4.55 K to 3.02 K and for  $z=0.017$  paramagnetic Curie temperature is equal to 2.63 K. In the case of  $\text{Sn}_{1-x-z}\text{Mn}_x\text{Eu}_z\text{Te}$  crystals such distinct tendency is not observed (see Table I). However, one needs to realize that obtained values of chemical composition as well as free carrier concentration are determined with quite large uncertainty.

The low temperature studies revealed the presence of paramagnet–ferromagnet phase transition in the case of  $\text{SnMnEuTe}$  as well as  $\text{PbSnMnEuTe}$  samples. Figure 2 and Figure 3 show the low temperature behaviour of real component of AC susceptibility  $\text{Re}(\chi)$  for several samples of studied  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  and  $\text{Sn}_{1-x-z}\text{Mn}_x\text{Eu}_z\text{Te}$  mixed crystals. A typical behaviour of a ferromagnet is observed. Both real and imaginary components of the susceptibility dramatically increase at the Curie temperature  $T_C$ . The Curie temperature was determined by the maximum slope of  $d\text{Re}(\chi)/dT$ . The values of  $T_C$  are approximately equal to the Curie-Weiss temperature  $\Theta$  determined from the high temperature susceptibility measurements. The low temperature measurements confirmed the above-described tendency for studied  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  crystals, i.e., the decrease of Curie temperature with the Eu content.

For the sample 809\_2 of  $\text{PbSnMnEuTe}$ , the ferromagnet to spin glass phase transition is observed. Figure 4 presents the characteristic behaviour of low temperature parts of the real and imaginary components of the susceptibility for the spin glass (809\_2) as well as for the ferromagnetic (809\_12) samples of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$ . In the case of ferromagnetic sample with the concentration of free holes equal to  $4.0 \times 10^{20} \text{ cm}^{-3}$ , the sharp transitions in both real and imaginary components of susceptibility occur. For the spin glass sample characterized by higher free hole concentration  $p = 1 \times 10^{21} \text{ cm}^{-3}$ , a cusp in  $\text{Re}(\chi)$  is visible at the freezing temperature  $T_f$ . The magnitude of the susceptibility at this cusp is much lower than the susceptibility of the ferromagnetic sample. A corresponding maximum in the out of phase of susceptibility  $\text{Im}(\chi)$  is observed at slightly lower temperature. The 809\_2  $\text{PbMnEuSnTe}$  sample shows an obvious characteristics of the spin glass–like phase. The cusp observed in the susceptibility  $\chi$  versus temperature  $T$  shifts to higher temperatures when the frequency  $f$  of the applied AC field is increased. This feature – the increase of the freezing temperature when the frequency is higher – was observed in many well-known canonical spin glass systems [5], [6], [7], [8]. The increase of  $T_f$  per decade of frequency is approximately constant, and dependence on frequency occurs in both real and imaginary parts of AC magnetic susceptibility. Figure 5 presents the frequency dependence of low temperature parts of real and imaginary

components of susceptibility for 809\_2 sample of PbMnEuSnTe. The relative shift of freezing temperature  $T_f$  per decade of frequency  $R = (\Delta T_f / T_f) \Delta \log f$  is equal to 0.021. The rate of the changes corresponding to maximum in imaginary part of susceptibility is higher:  $R = 0.048$ .

The values of  $R$  reported for known spin glass systems range from 0.005 (Cu) to 0.11 ( $\text{La}_{1-x}\text{Gd}_x\text{Al}_2$  [9]) and the rate of the change in  $\text{Im}(\chi)$  is the same as the rate of the change in  $\text{Re}(\chi)$ . The values of  $R$  reported for  $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$  are equal:  $R=0.027$  ( $x=0.04$ ) [10],  $R=0.022$  ( $x=0.008$ ) [11],  $R=0.027$  ( $x=0.022$ ) [11]. It appears that in the case of  $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$  mixed crystals the character of the spin glass phase does not depend on the manganese concentration. In the case of studied here  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  mixed crystals, comparable with Mn-based IV-VI magnetic semiconductors, the significant difference is visible in the inequality of frequency shift in  $\text{Re}(\chi)$  and  $\text{Im}(\chi)$ . It has to be noted that  $\text{Im}(\chi)$  in conducting media is distorted because of the eddy currents induced by AC magnetic field. Nevertheless, the obtained values differ from those obtained for analogous materials ( $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$ ), in particular the difference in the rate of frequency shift of cusp in real and imaginary part of susceptibility seems to be significant.

#### IV. QUALITATIVE ANALYSIS

We think that the most likely reason of the strong dependence of Curie temperature on the Eu content is a variation of the band structure parameters with the alloy composition. In the analysis of this problem the following points should be considered.

First, the Eu atom in PbMnSnTe matrix is a magnetic impurity with spin-only ground state:  $\text{Eu}^{2+}$  has  $S = 7/2$ . The electrons of the half-filled f-shell responsible for the moment are very weakly coupled to the band electrons. The coupling constant  $J_{s-f}$  is much smaller than  $J_{s-d}$  interaction. Thus, the indirect RKKY coupling between Eu ions is negligibly small. In addition, the Eu ion does not feel well any possible magnetization of the electronic system. As a result, one can not expect a substantial contribution of Eu magnetic ions to the average magnetization. Nevertheless, we should not totally exclude a small contribution from the s-f coupling between Eu atoms and carriers. Obviously, it would lead to a weak increase of the Curie temperature with the Eu content. Since the experiment shows the opposite behaviour, we can assume that the role of Eu as a magnetic impurity is negligibly small.

On the other hand, EuTe is known to be antiferromagnet. Thus, one can expect a transition from positive (Curie) to negative (Néel) temperature of magnetic ordering of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  alloy when changing the Eu content  $z$  from 0 to 1. However, the Eu-Eu interaction is not mediated by the free carriers, and, therefore, it is short ranged. For a small Eu content it leads to the antiferromagnetic ordering for a very small number of Eu-Eu pairs, which do not affect the interaction mechanism between the Mn ions.

If some of the Eu-Eu neighboring pairs are ordered antiferromagnetically, we can only expect that they do not contribute to the susceptibility, which is mostly related to the ferromagnetic Mn-Mn interaction. We conclude that the suppression of Curie temperature by a possible antiferromagnetic ordering of Eu-Eu pairs looks very unlikely.

The incorporation of Eu atoms can affect the properties of IV-VI compounds in a different way, which is not directly related to the magnetism of Eu ions. Eu is a component of the complex PbMnEuSnTe alloy, and one should consider a variation of the band parameters as a function of Eu content. For a qualitative analysis, let us assume here a simplified two-band model described by some phenomenological parameters. Note that the real energy spectrum of IV-VI compounds is rather complicated and one should account for the nonparabolicity and anisotropy of the energy bands. We use the following formula describing the indirect RKKY interaction between Mn ions, when the free carriers from several energy valleys are taken into account [12].

$$J_{\text{RKKY}}(R_{ij}) = N \frac{m^* J_{\text{sd}}^2 a_0^6 k_F^4}{32\pi^3 \hbar^2} \frac{\sin(2k_F R_{ij}) - 2k_F R_{ij} \cos(2k_F R_{ij})}{(2k_F R_{ij})^4} \quad (3)$$

where  $k_F$  is the Fermi wave number,  $m^*$  the effective mass of the carriers,  $J_{\text{sd}}$  the Mn ion-electron exchange integral,  $a_0$  the lattice constant,  $N$  the number of valleys of the valence band, and  $R_{ij}$  is the distance between the magnetic ions. If we take  $R_{ij}$  equal to the mean distance  $R$  between the magnetic ions (Mn), this formula gives the mean interaction energy between magnetic impurities which is roughly equal to the transition temperature  $T_C \approx J_{\text{RKKY}}(R)/k_B$ .

The energy spectrum in the L-points of Brillouin zone can be described by the Dirac model

$$E_L(k) = (\Delta^2 + v^2 k^2)^{1/2}, \quad (4)$$

where  $v$  is the band-coupling constant, for which we assume  $v = 5 \times 10^{-8}$  eV [13],  $\Delta = E_g/2$ , and  $E_g$  is the energy gap depending on the alloy composition.

There is another "heavy-hole" band with 12 minima in  $\Sigma$  points of the Brillouin zone. The energy spectrum of this band can be approximated as parabolic, and situated at the energy distance  $\epsilon_0$  from the bands described by equation (4)

$$E_\Sigma(k) = \epsilon_0 + \frac{\hbar^2 k^2}{2m_\Sigma^*}, \quad (5)$$

where  $m_\Sigma^* \simeq 3m_0$ , and  $m_0$  is the free electron mass. It is commonly known that the energy spectrum of  $\text{Pb}_{1-z}\text{Eu}_z\text{Te}$  alloy is very sensitive to the concentration of Eu. The energy gap  $E_g$  depends strongly on Eu content – ranging from 189.7 meV for  $z = 0$  (PbTe) to 248 meV for  $z = 0.013$  at the temperature  $T = 10$  K [13],  $dE_g/dz = 5.788$  eV at  $T = 10$  K for  $z < 0.05$  [14]. Considering the energy gap  $E_g$  dependence

on Sn content  $z$  of  $\text{Pb}_{1-x-y}\text{Mn}_x\text{Sn}_y\text{Te}$  alloy [13, 14], the following formula describing the energy gap dependence on the alloy composition in  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  crystals can be assumed:

$$E_g = 0.19(1 - y) - 0.3y + 5.788z \text{ [eV]} \quad (6)$$

In the present calculations the Mn concentration  $x$  was accepted as equal to 0.02.

We also assume [13], [15] that the composition dependence of  $\epsilon_0$  parameter has the following form:

$$\epsilon_0 = 0.8(1 - y) + 0.3y + 8z \text{ [eV]} \quad (7)$$

Using Eqs. 4 and 5 the hole concentration in L as well as in  $\Sigma$  valley can be found:

$$p_L = \frac{(E_F^2 - \Delta^2)^{3/2}}{3\pi v^3}, \quad (8)$$

$$p_\Sigma = \frac{1}{3\pi^2} \left[ \frac{2m_\Sigma^*}{\hbar^2} (E_F - \epsilon_0) \right]^{3/2}. \quad (9)$$

The Fermi energy  $E_F$  is determined by the equation:

$$4p_L + 12p_\Sigma = p_0, \quad (10)$$

which gives the total hole concentration  $p_0$  and takes into account the degeneracy of each valley. It is accepted here that  $p_0$  is equal to  $4 \times 10^{20} \text{ cm}^{-3}$ .

The Fermi momentum in the  $\Sigma$  band  $k_F^\Sigma = [2m_\Sigma^*(E_F - \epsilon_0)]^{3/2}$  can be found as a solution of Eqs. (8)-(10). Next, Eq. 3 with  $k_F = k_F^\Sigma$ ,  $R = (3a_0^3/4\pi x)^{1/3}$ ,  $a_0 = 6.5 \times 10^{-8} \text{ cm}$ ,  $N = 12$ ,  $J_{sd} = 1 \text{ eV}$  is used for  $T_C$  calculations. It implies that the main contribution to the RKKY interaction between Mn ions is related to the heavy holes in  $\Sigma$  bands.

The obtained  $T_C$  dependence on Eu concentration  $z$  for various values of Sn content ( $0.6 \leq z \leq 1$ ) is shown in Fig. 6. The experimental data (Curie temperature determined for samples with similar Mn content  $x \simeq 0.02$  and free hole concentration  $p \simeq 4 \times 10^{20} \text{ cm}^{-3}$ ) as well as calculated Curie temperature values divided by factor 1.95 are presented for comparison. As we see, the results of calculations within a simple two-band model can explain the observed experimentally tendency of Curie temperature decrease with Eu content. The obtained values of Curie temperature are higher than determined experimentally. However, it should be stressed that not all phenomenological parameters of the model are known precisely, and some simplifying assumptions are used. Nevertheless, the calculated dependence of Curie temperature on Eu content reflects very well the experimentally observed effect of the  $T_C$  decrease with Eu concentration  $z$ .



## V. SUMMARY

In this paper the results of magnetic and transport studies of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  multinary alloys are reported. The following results were obtained.

The presence of two types of magnetic ions (Mn and Eu) in IV-VI semiconductor matrix influences the magnetic properties of resultant magnetic semiconductor. The results of magnetic measurements show that the Curie temperature  $T_C$  as well as the Curie–Weiss temperature  $\Theta$  decrease with the increase of Eu content in  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples. The magnetic susceptibility measurements revealed also that Eu changes the spin glass dynamics in this material. The difference in the rate of frequency shift of cusp in the real and imaginary parts of susceptibility is visible. Such behaviour was not observed for Mn-based IV-VI magnetic semiconductors.

Our qualitative analysis shows that a variation of the band parameters with the alloy composition can be responsible for the observed strong dependence of the Curie temperature on Eu content. A simple two band model explains both the order of the transition temperature values and  $T_C$  dependence on Eu concentration. The calculated dependence of Curie temperature on Eu content reflects very well the experimentally confirmed effect of  $T_C$  decrease with Eu concentration  $z$ .

The observed dependence of the Curie temperature on Eu content clearly demonstrates that the magnetism of semiconductors can be effectively controlled by using an energy band structure dependence on alloy composition. The situation with several non-equivalent energy minima is not unique for IV-VI semiconductors. The similar effect exists also in Ge-Si alloys and in other semiconductors (like high-energy minima in GaAs). We believe that it can be used to increase the critical temperature of ferromagnetism in magnetically-doped semiconductors.

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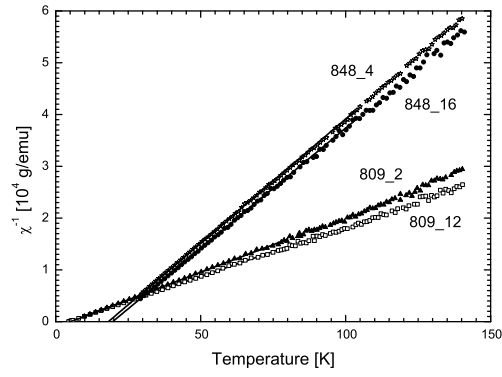


FIG. 1: The high temperature inverse AC susceptibility measured for several  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  and  $\text{Sn}_{1-x-z}\text{Mn}_x\text{Eu}_z\text{Te}$  samples (809\_2:  $x=0.031$ ,  $y=0.850$ ,  $z=0.003$ ; 809\_12:  $x=0.022$ ,  $y=0.760$ ,  $z=0.003$ ; 848\_4:  $x=0.061$ ,  $y=0.927$ ,  $z=0.0115$ ; 848\_16:  $x=0.050$ ,  $y=0.939$ ,  $z=0.011$ ). The solid lines correspond to Curie -Weiss law fits.

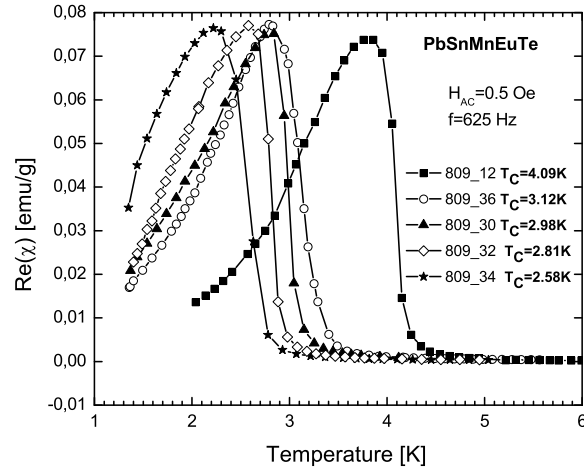


FIG. 2: The low temperature behaviour of real part of susceptibility for several  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples (809\_12:  $x=0.022$ ,  $y=0.760$ ,  $z=0.003$ ; 809\_36:  $x=0.025$ ,  $y=0.690$ ,  $z=0.013$ ; 809\_30:  $x=0.024$ ,  $y=0.710$ ,  $z=0.010$ ; 809\_32:  $x=0.026$ ,  $y=0.690$ ,  $z=0.014$ ; 809\_34:  $x=0.027$ ,  $y=0.680$ ,  $z=0.017$ ).

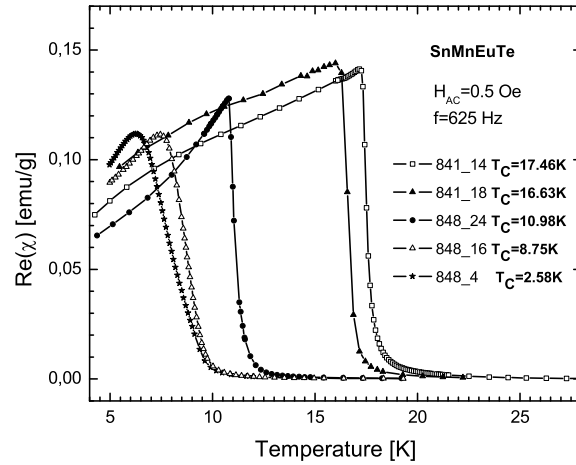


FIG. 3: The low temperature behaviour of real part of susceptibility for several  $\text{Sn}_{1-x-y}\text{Mn}_x\text{Eu}_y\text{Te}$  samples (841\_14:  $x=0.121$ ,  $y=0.873$ ,  $z=0.011$ ; 841\_18:  $x=0.128$ ,  $y=0.856$ ,  $z=0.014$ ; 848\_24:  $x=0.055$ ,  $y=0.930$ ,  $z=0.0175$ ; 848\_16:  $x=0.054$ ,  $y=0.939$ ,  $z=0.011$ ; 848\_4:  $x=0.058$ ,  $y=0.927$ ,  $z=0.011$ ).

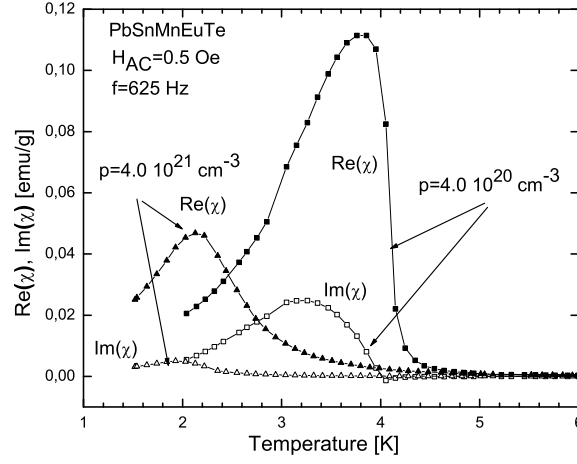


FIG. 4: The low temperature behaviour of both real  $Re(\chi)$  and imaginary  $Im(\chi)$  components of susceptibility for two samples of  $Pb_{1-x-y-z}Mn_xSn_yEu_zTe$ : 809\_2 ( $x=0.031$ ,  $y=0.850$ ,  $z=0.003$ ,  $p = 1 \times 10^{21} \text{ cm}^{-3}$ ) and 809\_12 ( $x=0.022$ ,  $y=0.760$ ,  $z=0.003$ ,  $p = 4 \times 10^{20} \text{ cm}^{-3}$ ). The typical ferromagnetic characteristics is observed for 809\_12 sample and spin glass behaviour for the sample with higher free hole concentration.

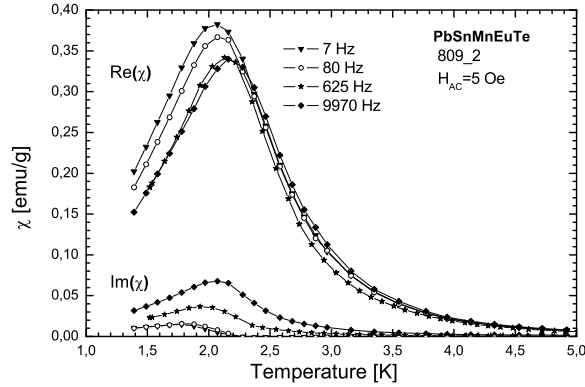


FIG. 5: The frequency dependence of real  $Re(\chi)$  and imaginary  $Im(\chi)$  components of susceptibility for the sample of  $Pb_{1-x-y-z}Mn_xSn_yEu_zTe$ : 809\_2:  $x=0.031$ ,  $y=0.850$ ,  $z=0.003$ ,  $p = 1 \times 10^{21} \text{ cm}^{-3}$ . The shift of the freezing temperature  $T_f$  towards higher temperatures with the frequency increase is clearly visible.

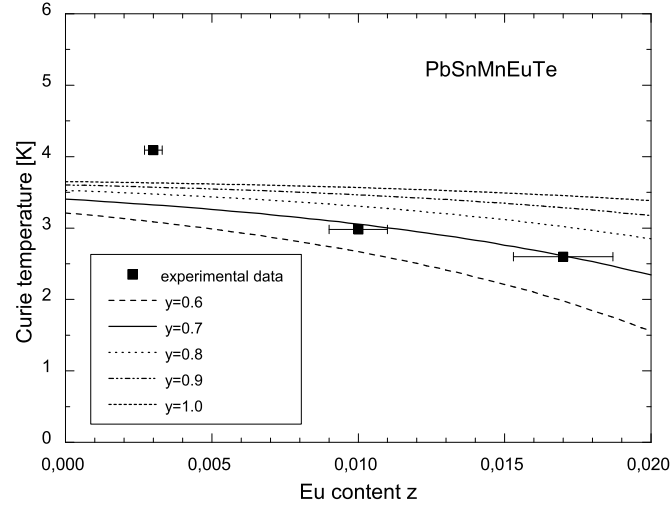


FIG. 6: Comparing of experimentally determined dependence of Curie temperature on Eu concentration  $z$  (for  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples with similar Mn content  $x \simeq 0.02$  and free hole concentration  $p \simeq 4 \times 10^{20} \text{ cm}^{-3}$ ) with the results of simple two-band model calculations. The calculated Curie temperature as a function of Eu content  $z$  for various values of Sn concentration  $0.6 \leq y \leq 1$  and Mn concentration  $x=0.02$  was divided by factor 1.95.

TABLE I: The results of magnetic and transport measurements for IV-VI mixed crystals.  $C$  is the Curie constant,  $\Theta$  is the paramagnetic Curie temperature (Curie-Weiss temperature),  $T_C$  is the Curie temperature,  $T_f$  is the freezing temperature,  $p$  is the free hole concentration obtained at room temperature.

sample number	$x$	$z$	$y$	$C$ [emu/g]	$\Theta$ [K]	$T_C$ [K]	$T_f$ [K]	$p$ [ $10^{21} \text{ cm}^{-3}$ ]
<b>Sn<sub>1-x-z</sub>Mn<sub>x</sub>Eu<sub>z</sub>Te</b>								
841_14	0.116	0.011	0.873	0.00215	19.65	17.46	-	1.40
841_18	0.131	0.013	0.856	0.00209	18.18	16.63	-	1.30
842_4	0.063	0.0045	0.932	-	-	10.90	-	1.40
842_8	0.068	0.003	0.929	-	-	13.07	-	1.56
842_14	0.070	0.007	0.923	-	-	15.23	-	1.56
842_20	0.091	0.009	0.900	0.00230	17.98	17.10	-	1.21
848_4	0.061	0.0115	0.927	0.00141	11.57	11.57	-	1.77
848_10	0.064	0.012	0.924	-	-	8.35	-	1.93
848_16	0.050	0.011	0.939	0.00149	11.02	8.75	-	1.24
848_22	0.065	0.018	0.917	-	-	10.75	-	1.37
848_24	0.051	0.019	0.930	0.00222	12.08	10.98	-	1.57
848_26	0.074	0.023	0.903	-	-	11.31	-	1.66
<b>Pb<sub>1-x-y-z</sub>Mn<sub>x</sub>Sn<sub>y</sub>Eu<sub>z</sub>Te</b>								
809_2	0.031	0.003	0.850	0.00047	5.16	-	2.0	1.01
809_4	0.030	0.002	0.850	0.00050	4.88	-	-	0.501
809_10	0.030	0.003	0.780	0.00050	4.74	4.13	-	0.601
809_12	0.022	0.003	0.760	0.00052	4.55	4.09	-	0.401
809_30	0.024	0.010	0.710	0.00080	3.02	2.98	-	0.425
809_30 ann	0.024	0.010	0.710	0.00080	4.16	3.55	-	0.822
809_32	0.026	0.014	0.690	0.00082	2.89	2.81	-	0.325
809_34	0.027	0.017	0.680	0.00090	2.60	2.60	-	0.449
809_36	0.025	0.013	0.690	0.00077	3.13	3.12	-	0.318
<b>Pb<sub>1-x-z</sub>Mn<sub>x</sub>Eu<sub>z</sub>Te</b>								
793_2	0.010	0.000	-	0.00039	-0.93	-	-	-
793_4	0.010	0.001	-	0.00038	-0.69	-	-	-
793_4	0.010	0.001	-	0.00038	-0.69	-	-	-
793_6	0.009	0.009	-	0.00051	-1.12	-	-	-
793_10	0.005	0.004	-	0.00053	-0.42	-	-	-
793_12	0.007	0.003	-	0.00059	-0.39	-	-	-
793_14	0.005	0.005	-	0.00086	-0.41	-	-	-

TABLE II: The lattice constant  $a_0$  of  $\text{Pb}_{1-x-y-z}\text{Mn}_x\text{Sn}_y\text{Eu}_z\text{Te}$  samples determined by the standard powder X-ray measurements and the values of the calculated lattice constant of  $\text{Pb}_{1-x-y}\text{Mn}_x\text{Sn}_y\text{Te}$   $a$  [3] with similar content of Mn and Sn.

# of the sample	$x$	$z$	$y$	$a_0$ [Å]	$a$ [Å]
809_2	0.031	0.0027	0.85	6.3130	6.2866
809_4	0.030	0.0016	0.85	6.3237	6.2876
809_12	0.022	0.003	0.76	6.3375	6.3113
809_28	0.020	0.007	0.73	6.3563	6.3309
809_36	0.025	0.013	0.69	6.3427	6.3311